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Catalytic oxidation of NO into NO₂ was studied over activated carbon fibers at room temperature to trap the unreacted NO as well as the oxidized product as the acid or salts. The heat-treatment of pitch based activated carbon fiber was found to enhanced markedly the activity to allow the conversion of 82% in dry and 25% in wet air at 25°C by W/F of $1.0 \times 10^{-2} \text{ g} \cdot \text{min} \cdot \text{ml}^{-1}$. The strong retardation by humidity on the activity of as-received fiber was moderated by the heat-treatment. The rate of oxidation was examined by varying concentration of NO, H₂O and NO₂. The catalytic activities of other fibers were also examined in dry and wet air.

Introduction

NO in flue gas or even in the atmosphere has been continuously expected to be removed or converted into harmless species more extensively and more efficiently. Selective catalytic reduction of NO in flue gases from various sources has been performed in a commercial scale, using vanadium on TiO₂ catalyst in a honey comb from at a temperature range of 300 to 400°C, where the complete decomposition of (NH₄)₂SO₄ is achieved.¹⁾ Although such a SCR process appears proven and established, there remain several problems such as a high reaction temperature which requires reheating, large volume of reactor and necessity of reductant ammonia. The process is not applicable to NO from mobile sources or in very low concentration at ambient temperature as observed in urban areas.

Low temperature SCR processes have been explored around 100-150°C using zeolite and active carbon as the catalysts and ammonia as the reductant.²⁾ Complete removal of SO₂ before SCR is strictly necessary because (NH₄)₂SO₄ tends to plug the reactor as well as the catalyst bed. The present authors have proposed such a process catalyzed by activated carbon fiber (ACF) to reduce NO of 10ppm at room temperature in the atmosphere.^{3,4)} However, severe retardation by humidity, necessity of ammonia and further activation of ACF with H₂SO₄ may increase the cost to be unacceptable.

In the present paper, we describe the catalytic activity of activated carbon fibers and their heat-treated ones for the oxidation of NO in flue or air to be captured as the nitric acids or salts. Such an oxidation catalyzed by active carbon has been reported for a long time.^{5,6,7)} The unsatisfactory activity and strong retardation by humidity so far restricts further development in the practical application.

The present authors have revealed that the surface properties of activated carbon fiber can be controlled by the selection of precursor, activation conditions and post-modification such as heat-treatment as well as chemical treatment. Hence we examined in the present study the catalytic activity of pitch and PAN based activated fibers and their heat-treated ones to explore the high humidity-resistive activity. Very preliminary trials to capture the oxidized nitric species in water and aqueous bases are also included.

Experimental

Pitch based (OG-5A, -10A, -20A) and PAN-based (PAN-FE300) active carbon fibers (ACFs) were supplied by Osaka Gas and Toho Rayon, respectively in yarn forms. Their properties are summarized in Table 1.

The fibers were heat-treated in N₂ at 200 to 1000°C for 4h. Properties of the fibers heat-treated at 800°C (H800) are listed also in Table 1. Oxidation of NO was performed in a fixed bed U-shaped flow type reactor. The weight and length of fiber bed, flow rate, the concentrations of NO in N₂ containing 4-15% O₂, and reaction temperatures were 0.5g, 70mm, 50ml · min⁻¹, 380ppm, and 25-125°C, respectively. Air was humidified at 25°C. Reactant and product gases were analyzed by NOX meter (ECL-77A, YANAGIMOTO Co., Ltd.).

The oxidized gas was washed in a washing bottle after the reaction before the analyzer to examine the capture of NO₂ and remaining NO. Water and aqueous KOH (1mol/l) were placed in the bottle by the depth of 70mm (100ml).

Results

1. Catalytic activity of a pitch based ACF, OG-5A

Figure 1 illustrates the compositional change of a model gas at the outlet of the reactor at 25°C over as-received OG-5A. NO in dry air decreased its concentration from 380ppm to 75ppm by passing through the OG-5A for the first 2h and then increased it gradually to 170ppm by 20h. Up to this time, no nitric species except for NO was found in the outlet gas, adsorption of the species being suggested although so far their form is not identified.

At 20h after the gas flow started, NO₂ started to be found in the outlet gas. The concentration of NO₂ steadily increased, while NO both found and missed, being calculated from N balance, decreased. At 40h, the concentrations of NO and NO₂ became stationary to be 100 and 300ppm, respectively, N balance being now obtained. Such stationary conversions continued at least for 40h.

Increasing humidity in the air decreased the adsorption amount of N species and conversion of NO into NO₂ at the stationary states, shortening the time to reach the stationary state. Although the retardation of humidity was slight when the humidity was below 60%, humidity above 80% retarded very markedly and humidity of 100% decreased severely the NO conversion into NO₂ to

only null.

2. Influence of heat treatment

Figure 2 illustrates the activity of OG-5A heat treated at 800°C (OG-5A-H800) for the oxidation of NO at 25°C. Although the profile for NO adsorption and oxidation over OG-5A-H800 was similar to that over as-received OG-5A, the activity was certainly much higher by the heat treatment. The stationary conversion of NO into NO₂ in dry air increased to 80 % by the same W/F. The humidity in air reduced the conversion to 87% at 60% r.h., 55% at 80%r.h., 15% at 100%r.h.. Such reduction was certainly much less with the heat treated OG-5A than that with the as-received one. The activity at 80%r.h. should be noted.

Figure 3 summarizes the stationary conversions of NO into NO₂ over OG-5A heat treated at 400 to 1000°C. The heat treatment increased slightly the activity in dry air, providing the largest activity at 800°C. Either lower or higher temperature decreased the conversion. The increase of activity by the heat treatment at 800°C was most marked when the relative humidity was 80%. Activity increase by four times in comparison with that of as-received OG-5As was very significant. Further higher humidity reduced the conversions over all OG-5A regardless of the heat treatment. Nevertheless OG-5A-H800 exhibited the highest conversion of only 15%. Although the activity increase may be remarkable even under 100%r.h. because the as-received OG-5A exhibited no activity at all under the same conditions.

3. Influences of reaction conditions

Figure 4 summarizes the influences of relative humidity on the conversion of NO over as-received and a heat treated OG-5A-H800 ones. Although the humidity reduced the conversion slightly below 60% but severally above 60%r.h. especially over 80%r.h., the marked influence of the heat treatment was observed at 80%r.h.. (The activity under 100%r.h. was composed in more detail, varying the W/F.)

The oxygen concentration above 7% provided the same conversion of NO over OG-5A-H800 regardless of relative humidities at 25°C.

Figure 5 illustrates the conversion of NO in a temperature range of 30 to 125°C over OG-5A-H800 at 4% O₂ in dry and humid airs. Air was humidified at 30°C to carry 30.4g/m³ H₂O. Hence, the relative humidity decreased at the higher reaction temperature. The conversion in dry air decreased monotonously with rising the reaction temperature.^{5,6)} The decrease was marked above 50°C. In contrast, the conversion increased with rising temperature upto 75°C in the humid air. The conversion decreased above 75°C as observed in dry air. Higher oxygen concentration of 15% increased more markedly the conversion in humid air at 75°C.

Table I summarized the conversions of NO into NO₂ over PAN, pitch ACFs and their heat treated ones. OG-5A exhibited the largest activity in dry air among the as-received ones. The larger surface areas of pitch ACFs tended to show lower activity. Pitch ACF was more active than PAN-ACF. The heat treatment at 800°C enhanced the activity of all ACFs, OG-5A-H800 exhibiting the largest activity in dry air. Superiority of pitch ACF was more marked in wet air of 80%, where OG-5A-H800 and PAN-FE-300-H800 exhibited the conversions of 65 and 38%, respectively.

4. Capture of Oxidized NO

Figure 1 illustrates the extent of captured NO₂ and NO at the outlet of the reactor after the catalytic oxidation of NO over OG-5A as-received. Under the conditions described, NO of 380ppm was oxidized into NO₂ by the conversion of 73% as described above. Water in the washing bottle (100ml, depth of water 70mm.) captured 70% of produced NO₂, passing remaining NO₂ and unreacted NO. Aq.KOH (1mol/l) of 100ml captured all NO₂ produced and 58% of unreacted NO, a removing 91% of NO of the inlet gas. More efficient contact of gas with water or aq.KOH can remove more NO as well as NO₂.

Discussion

The present paper describes the significant catalytic activity of pitch based activated carbon fiber, especially after the heat treatment at 800°C, for the oxidation of NO into NO₂ at 25°C, which is captured rather easily with water or aq. basic solution. Two points may be worthwhile for discussion.

The first point is related to the retardation by humidity as reported in the past^{5,6)}. The important feature is that the heat treatment improved the resistivity against the humidity, allowing the significant activity at room temperature in air of humidity up to 80%, where the ACF as-received lost the activity very severely.

The hydrophobic surface may be induced on the particular ACF surface of potentially high graphitizability. The removal of oxygen functional groups in forms of CO or CO₂ is well established for the ACF surface.⁸⁾ Certain graphitization may be achieved by such a treatment, although the ACF experienced such a temperature in the activation stages. The preference of the pitch based fiber to PAN based fiber is ascribed to the graphitization potential of the former fiber.

Second point is related to the active site for the oxidation on the ACF surface. The heat treatment appears to induce more number or more active sites for the oxidation of NO as well as SO₂ as described in a preceding paper.^{9,10)} The site is induced by the liberation of CO and CO₂ in contrast to the expectation that the oxidation active site is connected to the oxygen functional group. Unidentified site for oxidation appears to be introduced by the heat treatment. Surface carbon of unsaturation in its valence may be induced.

The interesting point is that PAN and pitch based ACFs exhibited the reverse order of catalytic activity for the oxidation of SO₂ and NO.^{11,12)}

Different ways of H₂O intervention in the two oxidation reactions may cause the different activity in humid air. The activity in dry air may reflect the different interactions of such substrate with the ACF-surface. Detail characterization of surface is necessary.

In conclusion, the combination of PAN-ACF and pitch ACF after the heat treatment at 800°C may allow the oxidative removal of both SO₂ and NO at room temperature in their acid forms, providing a base for novel technology for treatment of both flue and atmosphere. The successive application of both ACFs can recover H₂SO₄ and HNO₃, separately.

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Table 1 Some Properties of ACFs

ACFs	Ultimate analysis (wt%)						Surface area (m ² /g)	Pore vol. (ml/g)
	C	H	N	O	S	Ash		
OG-5A(As-received)	89.6	1.1	0.7	8.3	tr	0.3	480	0.25
OG-10A(As-received)	91.6	0.9	0.5	6.7	tr	0.3	710	0.37
OG-20A(As-received)	93.9	0.9	0.3	4.6	tr	0.5	1550	0.81
PAN-EF300(As-received)	83.4	0.9	4.7	9.2	0	1.8	875	0.46
OG-5A-H800 ^{a)}	92.1	1.0	0.5	5.8	0	0.6	450	0.23
OG-10A-H800	94.0	0.8	0.4	4.4	0	0.4	620	0.32
OG-20A-H800	95.8	0.6	0.3	2.8	0	0.5	1320	0.68
PAN-FE300-H800	86.9	0.7	3.6	5.8	0	3.0	810	0.42

a) Calcined at 800°C in N₂

Table 2 Catalytic Activities of ACFs for NO Oxidation in Dry and Humidified Carrier

ACFs	NO conversion (%)		
	r.h.=0%	r.h.=60%	r.h.=80%
OG-5A(As-received)	73	58	18
OG-10A(As-received)	71	56	14
OG-20A(As-received)	64	49	16
PAN-EF300(As-received)	60	43	4
OG-5A-H800	82	74	65
OG-10A-H800	80	71	56
OG-20A-H800	75	66	51
PAN-FE300-H800	71	57	38

NO: 380ppm (N₂ Balance), O₂: 4.0%

W/F=1×10⁻² g · min/ml, W=1.0g

Reaction temp.: 25°C

Conversion was observed 40h after the reaction started.

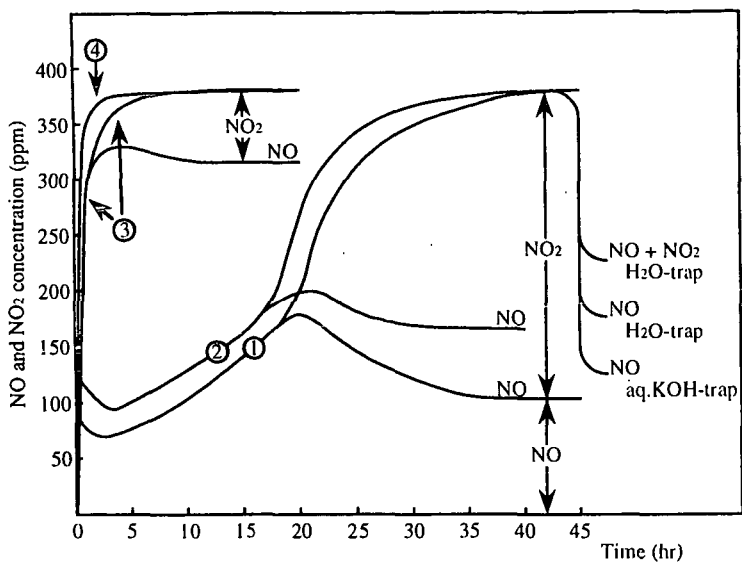


Fig.1 Oxidation of NO into NO₂ over As-received Pitch Based ACF OG-5A

ACF : OG-5A(As-received), W=1.0g
 NO : 380ppm (N₂ Balance), O₂ : 4.0%
 W/F=1 × 10⁻² g · min/ml, Reaction temp. : 25 °C
 Relative humidity : ① 0% ② 60% ③ 80% ④ 100%
 Outlet gas passed through washing a bottle.
 H₂O : 100ml, depth 70mm, T=25 °C
 aq.KOH(1mol) : 100ml, depth 70mm, T=25 °C

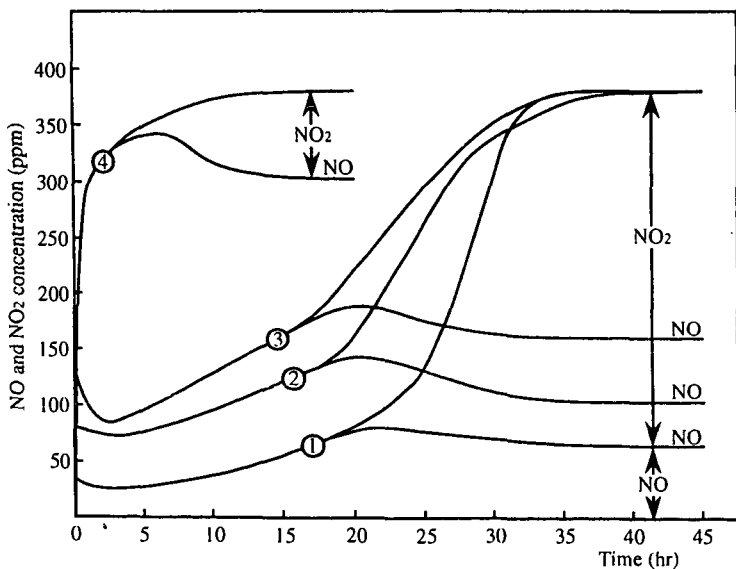


Fig.2 Oxidation of NO into NO₂ over OG-5A Heattreated at 800 °C (OG-5A-H800)

ACF : OG-5A-H800, W=1.0g
 NO : 380ppm (N₂ Balance), O₂ : 4.0%
 W/F=1 × 10⁻² g · min/ml, Reaction temp. : 25 °C
 Relative humidity : ① 0% ② 60% ③ 80% ④ 100%